

# PATENT SPECIFICATION

(11) 1 523 308

1 523 308

(21) Application No. 51567/75 (22) Filed 17 Dec. 1975  
(31) Convention Application No. 2 459 765  
(32) Filed 18 Dec. 1974 in  
(33) Fed. Rep. of Germany (DE)  
(44) Complete Specification published 31 Aug. 1978  
(51) INT CL<sup>2</sup> C07C 125/04; C08G 65/32  
(52) Index at acceptance

C2C 1175 200 20Y 220 221 225 226 227 22Y 30Y 340 342  
34Y 360 361 364 366 368 36Y 577 627 62X 637 647  
70Y 71Y 796 79Y KA KB

C3R 27K8D 38B1A 38B3D 38D1A3 38D7B 38N1H 38N1M1  
38N1MX 38N1S 38N4



## (54) MANUFACTURE OF CARBAMATES

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention relates to a process for the manufacture of a carbamate by reaction of an alcohol with urea in the presence of nickel.

10 Houben-Weyl, Methoden der Organischen Chemie, volume 8, page 190 et seq. discloses that alcohols may be reacted with urea to give carbamates. The yields from the process are unsatisfactory, even using a fairly long reaction time and a large excess of alcohol, since by-products, e.g., biuret, allophanic acid esters and cyanuric acid, are produced. It is true that the yields can be improved by using zinc acetate, lead acetate or cobalt chloride (Z. Naturforsch., 1 (1946), 520) or using metal salts and metals, of which zinc dust, zinc oxide, vanadium pentoxide, tin(IV) chloride and tin(II) chloride, zinc salts, manganese acetate, chromium acetate, lead acetate, uranyl acetate, silver nitrate and copper sulfate have been given as examples (German Patent 752,127). However, the carbamates thus obtained still contain a certain proportion of the above by-products, which precludes their use in all syntheses which require starting materials of the highest purity. Thus, e.g., such crude carbamates cannot be used directly for the manufacture of dimethylol compounds which are employed as finishing agents for chlorine-resistant finishing of textiles, and instead must first be purified by renewed distillation, or recrystallization.

15 20 25 If the method of the above German patent—which does not mention nickel salts—is followed, and the metal catalysts described are used, with glycol monoethers in place of monohydric alkanols as the starting materials, it is not only the purity of the end product but also, in many cases, its yield which is unsatisfactory. The Table which follows shows the results obtained in reacting urea with methylglycol (molar ratio 1:3) to give methoxyethylene-carbamate.

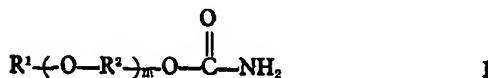
## TABLE

(Reaction temperature 130°C, reaction time 25 hours)

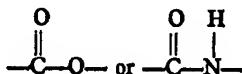
Catalyst	Amount of catalyst based on urea (% by weight)	Yield based on urea (% of theory)
Boron trifluoride	1	50
Aluminum acetate	5	55
Manganese sulfate	5	57
Sodium aluminate	5	58
Sodium tetrafluoborate	1	63
Copper filings	5	70
Tin (IV) chloride	5	85

Further, German Published Application 1,643,635 discloses the manufacture of hydroxyethylene-carbamate ethers by reaction of ethylene glycol monoethers with urea at from 100 to 150° C. in the presence of nickel compounds. It is true that the yields are 94% of theory, but, as shown by the Examples, reaction times of at least 21 hours are needed. Nickel compounds, in the said application, means nickel salts; nickel chloride is employed in the Examples.

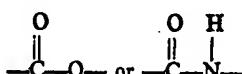
We have found that a carbamate of the formula



where  $R^1$  is an aliphatic, cycloaliphatic or araliphatic radical which may be interrupted by one or more



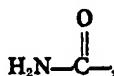
groups and/or oxygen atoms,  $R^2$  is an aliphatic radical of at least 2 carbon atoms which is optionally interrupted by one or more



groups and/or oxygen atoms, or is



where the  $R^3$ 's may be identical or different and each is a cycloaliphatic, araliphatic or aromatic radical, and  $n$  is an integer from 2 to 6, and  $m$  is 0 or a positive integer, or  $R^1$  is



or phenyl or—if  $m$  is a positive integer—hydrogen, may be obtained in an advantageous manner by a process wherein an alcohol of the formula



II

where  $R^1$ ,  $R^2$  and  $m$  have the above meanings, is reacted with urea in the presence of an ion exchanger containing nickel.

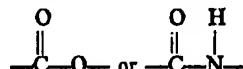
It is to be understood that, when  $R^1$  in the formula II is hydrogen or  $R^1$  or  $R^2$  (or both) in that formula includes one or more OH groups, the symbol (or symbols) in question in formula I need not be identical but may denote the carbamate corresponding to the alcohol (or a partial carbamate in the case where more than one such OH group is present initially). It is, however also possible for such an OH group to be present in the product.

When using methylglycol, the reaction can be represented by the following equation:

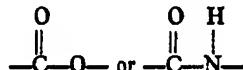


Compared to the conventional process, the process of the invention is able to give a large number of carbamates more simply and more economically, in better yield and purity and with better space-time yield. Compared to the process disclosed in German Published Application 1,643,635, the new process offers advantages in that the reaction time is substantially reduced and is in general from 5 to 10 hours and the space-time yield is increased by a factor of 3—4. In the light of the cited publications, it is surprising that the process of the invention gives a large number of carbamates by a simple method, in better yield and purity and without formation of by-products. Carbamates can be obtained by the new process which conform to the highest standards of purity and can, e.g., be reacted, without prior purification, with formaldehyde to give the above dimethylol compounds used for chlorine-resistant textile finishes, thereby offering a labor-saving and more economical method of manufacture of assistants, e.g. ordinary textile finishes and resin textile finishes. Particularly in view of German Published Application 1,643,635, it would have been expected that the new process would not give better yields and better purity and would even give poorer results, since—contrary to the teaching of the said published application, according to which only nickel salts should be used, in amounts of from 0.1 to 5% by weight based on urea—the process of the invention is carried out with cation exchangers and the nickel bonded as a cation to the exchanger. After completion of the reaction, neither nickel nor dissolved nickel salts remain in the reaction mixture and such salts can thus, in the light of the process described in German Published Application 1,643,635, not react with the carbamate formed so as to induce a reverse reaction or the formation of undesirable by-products. The process according to the invention offers a further advantage that the ion exchangers containing nickel can be re-used as frequently as desired without regeneration.

The starting materials used are urea and alcohols of the formula II. Preferred starting materials II and, accordingly, preferred end products I, are those where  $R^1$  is alkyl of 1 to 18, preferably of 1 to 10, and especially of 1 to 7, carbon atoms which may be interrupted by several, in particular by one,



group and/or by one or more oxygen atoms, preferably by from 1 to 6 and especially 1 or 2 oxygen atoms, or  $R^1$  is cycloalkyl or 5 or 6 carbon atoms or aralkyl of 7 to 12 carbon atoms,  $R^2$  is alkylene of at least 2, preferably at least 4 carbon atoms and not more than 18, preferably not more than 10 and especially not more than 7, carbon atoms which may be interrupted by several, or in particular by one,



group and/or by oxygen atoms, preferably by from 1 to 6 and especially 1 or 2 oxygen atoms, advantageously the radical

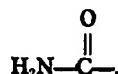


where the R<sup>4</sup>'s are identical or different and each is hydrogen or alkyl of 1 to 7 carbon atoms and n is an integer from 2 to 6, preferably 2, 3 or 4, or R<sup>2</sup> is the radical



5 where the R<sup>3</sup>'s are identical or different and each is cycloalkyl of 5 or 6 carbon atoms or aralkyl of 7 to 12 carbon atoms or phenyl, and n is an integer from 2 to 6, preferably 2, 3 or 4, and m is 0 or an integer from 1 to 50, preferably from 1 to 28, and especially 0, 1, 2, 3, 9 or 18, or R<sup>1</sup> is

5



10 phenyl or—if m is not less than 1—hydrogen. If m is greater than 1, several R<sup>2</sup>'s, which may be identical or different, are present. The above radicals may further be substituted by groups which are inert under the reaction conditions, e.g. alkyl or alkoxy each of 1 to 4 carbon atoms, carbamoyl, carbalkoxy of 2 to 6 carbon atoms, or carbamato, or by hydroxyl groups which may or may not react with urea in the course of the reaction to introduce further carbamate groups.

10

15 The urea may be employed in the reaction in a stoichiometric amount or less, preferably in an amount of from 0.5 to 1 mole per mole of starting material II when it contains one free hydroxyl group. If 2 hydroxyl groups are present, the monocarbamate is suitably obtained if from 0.5 to 1 mole of urea is used per mole of starting material II, mixtures of monocarbamate and dicarbamate are obtained if larger amounts of urea, of up to 2 moles per mole of starting material II, are employed, and the dicarbamate alone is obtained if from 2 to 2.5, preferably from 2 to 2.2, moles of urea are employed per mole of starting material II. Analogously, in the case of higher polyhydroxy-alcohols, it is possible, by using stoichiometric or correspondingly reduced amounts of urea, to produce monocarbamates, dicarbamates, tricarbamates, tetracarbamates and higher polycarbamates in the pure form or as a mixture of carbamates, whereof the components depend on the molar ratio of the starting materials and the number of hydroxyl groups in the alcohol II. Thus, e.g., depending on the molar ratio of urea, the alcohols shown below can give the following corresponding carbamates:

15

20

20

25

25

Alcohol	Carbamate
HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCONH <sub>2</sub> and H <sub>2</sub> NCOOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCONH <sub>2</sub>
HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCONH <sub>2</sub> and H <sub>2</sub> NCOOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCONH <sub>2</sub>
HOCH <sub>2</sub> CH=CH—CH <sub>2</sub> OH	HOCH <sub>2</sub> CH=CH—CH <sub>2</sub> OCONH <sub>2</sub> and H <sub>2</sub> NCOOCH <sub>2</sub> CH=CHCH <sub>2</sub> OCONH <sub>2</sub>
HOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	HOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCONH <sub>2</sub> and H <sub>2</sub> NCOOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCONH <sub>2</sub>

Alcohol	Carbamate
$  \begin{array}{c}  \text{CH}_3 & \text{CH}_3 \\    &   \\  \text{HOCH}_2-\text{C}-\text{COOCH}_2-\text{C}-\text{CH}_2\text{OH} & \text{CH}_3 & \text{CH}_3 \\    &   \\  \text{CH}_3 & \text{CH}_3  \end{array}  $	$  \begin{array}{c}  \text{CH}_3 & \text{CH}_3 \\    &   \\  \text{HOCH}_2-\text{C}-\text{COOCH}_2-\text{C}-\text{CH}_2\text{OCONH}_2, \\    &   \\  \text{CH}_3 & \text{CH}_3  \end{array}  $
	$  \begin{array}{c}  \text{CH}_3 & \text{CH}_3 \\    &   \\  \text{H}_2\text{NCOOCH}_2-\text{C}-\text{COOCH}_2-\text{C}-\text{CH}_2\text{OH} \text{ and} \\    &   \\  \text{CH}_3 & \text{CH}_3  \end{array}  $
	$  \begin{array}{c}  \text{CH}_3 & \text{CH}_3 \\    &   \\  \text{H}_2\text{NCOOCH}_2-\text{C}-\text{COOCH}_2-\text{C}-\text{CH}_2\text{OCONH}_2 \\    &   \\  \text{CH}_3 & \text{CH}_3  \end{array}  $

Preferred starting materials II are:

$\text{C}_4\text{H}_9\text{OH}$ ,  $\text{C}_{10}\text{H}_{21}\text{OH}$ ,  $\text{C}_{17}\text{H}_{35}\text{OH}$ ,  $\text{C}_6\text{H}_{13}\text{OH}$ ,  $\text{C}_6\text{H}_5\text{OH}$ ,  $\text{C}_6\text{H}_5\text{OCH}_2\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OCH}_2-\text{CH}_2\text{OH}$ ,  
 $\text{C}_2\text{H}_5\text{OCH}_2-\text{CH}_2\text{OH}$ ,  $\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_6\text{H}_5\text{OCH}_2-\text{CH}_2\text{OH}$ ,  
 $\text{C}_2\text{H}_5\text{OCH}_2-\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_6\text{H}_5\text{OCH}_2-\text{CH}_2\text{CH}_2\text{OH}$ ,  
5  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$  and  

$$\begin{array}{c}
 \text{CH}_3 & \text{CH}_3 \\
 | & | \\
 \text{HOCH}_2-\text{C}-\text{COOCH}_2-\text{C}-\text{CH}_2\text{OH} \\
 | & | \\
 \text{CH}_3 & \text{CH}_3
 \end{array}$$

However, it is also possible to use, e.g., the following alcohols as starting materials II: 1,3,5-trihydroxypentane, 2-acetoxy-1-ethanol, 2-acetamido-1-ethanol, cyclopentyl alcohol, phenylethyl alcohol, decyl alcohol, octadecyl alcohol and the following alcohols, which are either unsubstituted or substituted, at the  $\omega$ -hydroxyl group, by the radicals specified or the radicals described in connection with the above preferred individual alcohols II: hydroxypropyl-(1) alcohol, hydroxypropyl-(2) alcohol, hydroxy-n-butyl-(1) alcohol, hydroxy-n-buten-(2,3)-yl-(1) alcohol, hydroxyethoxyethyl-(1) alcohol, triethylene glycol, hydroxy-pivalato-(3)-neopentyl-(1) alcohol,  $\alpha$ -hydroxyacetamido-(3)-neopentyl-(1) alcohol,  $\omega$ -hydroxydecyl-(1) alcohol,  $\omega$ -hydroxy-7,4,6-triethyl-octanyl-(1) alcohol, 2-hydroxy-2-cyclohexylethyl-(1) alcohol, 2-hydroxy-2-benzylethyl-(1) alcohol, 2-hydroxy-2-phenylethyl-(1) alcohol and 6-hydroxyhexyl-(1) alcohol.

The reaction is as a rule carried out at from 100 to 160° C., preferably at from 125 to 150° C., under atmospheric or superatmospheric pressure, continuously or batchwise. In general, the starting material II also serves as the reaction medium though if appropriate, organic solvents which are inert under the reaction conditions may be used, e.g. aromatic hydrocarbons such as benzene, toluene, ethylbenzene, o-, m- and p-xylene, isopropylbenzene and corresponding mixtures. The amount of solvent used is suitably from 200 to 10,000% by weight, preferably from 200 to 1,000% by weight, based on starting material II. If the alcohol II alone is the reaction medium, an appropriate additional amount thereof is added to the starting mixture.

The reaction is carried out in the presence of ion exchangers—as a rule acid ion exchangers, and preferably acid synthetic ion exchange resins—which contain nickel. Such exchangers include all the cation exchangers described in Houben-Weyl, Methoden der Organischen Chemie, volume I/1, page 528, Table 3. Exchangers of strong to medium acidity, e.g. phenolic resins or polystyrenesulfonic acid resins, or exchangers containing appropriate acid resins, e.g. bifunctional condensation resins, are used preferentially. It is also possible to use polystyrenephosphonic acid resins, polystyrenephosphinic acid resins, resorcinol resins and aliphatic or aromatic carboxylic acid resins. The above cation exchangers are commercially available, e.g. under the Registered Trade Marks Amberlite, Lewatit, Lewasorb and Amberlyst, specific

examples being Amberlyst 15, Amberlite 200, Lewatit CA 9259, Lewatit S 100 and Lewasorb V 100. Before the reaction, the exchangers are charged with nickel in accordance with conventional methods, suitably by a treatment with solutions, advantageously aqueous solutions, of nickel salts. Suitable nickel salts are nickel chloride, nickel acetate, nickel bromide, nickel nitrate and, preferably, nickel sulfate. The nickel compounds may also be in the form of corresponding hydrates, e.g. nickel chloride hexahydrate. However, nickel phosphate, nickel carbonate, nickel bicarbonate, nickel borate, nickel oxalate and nickel propionate may also be used. Before treating the exchanger, the water which may be present in the exchanger can be removed by passing organic solvents, such as alcohols, e.g. methanol, ethers, e.g. glycol monomers or tetrahydrofuran, or acetals, e.g. formaldehyde, through the exchanger. Preferably, the exchanger is activated, prior to the treatment with the nickel salt, by means of an acid, suitably sulfuric acid, hydrochloric acid or the acid corresponding to the anion of the nickel salt. The exchanger is advantageously first left for from 10 to 30 minutes under or in water at from 15 to 40° C. and is then activated for from 10 to 60 minutes with acid, suitably in the form of an aqueous solution of from 2 to 15 per cent strength by weight, at from 15 to 40° C., after which the exchanger is washed with water until neutral.

The treatment of the ion exchanger with the nickel salt solution is suitably carried out at from 10 to 50° C., preferably from 20 to 30° C. It may be carried out under atmospheric or superatmospheric pressure, batchwise, e.g. by a stirring-in or batch method, or, preferably, continuously, e.g. in exchange columns, in a fixed bed, flowing bed or fluidized bed in tray columns. Suitably, nickel salt solutions of from 5 to 50 per cent strength by weight are used, the treatment times being from 10 to 60 minutes. After the treatment, it is advantageous to rinse the exchanger with water until the wash liquor, or the wash liquor issuing from the exchange column, gives a neutral reaction, and then to wash the exchanger for from 10 to 60 minutes, at from 15 to 40° C., with one of the above inert solvents or an alcohol, in the case of liquid alcohol II preferably with the particular alcohol II which is to be used (for the reaction), until the exchanger is substantially free from water. Suitably, one part by weight of exchanger is charged with from 0.01 to 0.2, preferably from 0.02 to 0.1, and especially from 0.02 to 0.08, part by weight of nickel, and from 0.01 to 0.25, preferably from 0.02 to 0.1, part by weight of exchanger is then used per part by weight of urea.

The reaction may be carried out as follows: a mixture of urea, starting material II, exchanger and, where used, the solvent, is kept for from 7 to 12 hours at the reaction temperature. It is advantageous to remove the ammonia produced during the reaction from the reaction solution by passing nitrogen through the latter. The reaction mixture is then cooled and filtered. The end product is isolated from the filtrate by conventional methods, e.g. by distillation. The unconverted starting material II and the ion exchanger, containing nickel, which has been filtered off, can be returned to the reaction.

The compounds which may be manufactured by the process of the invention are valuable starting materials for the manufacture of textile finishing agents, dyes and plant protection agents. For example, they can be methylolated to give textile finishing agents which give a good wrinkle-resist effect and finishing effect together with a softer, harder or fuller hand, depending on the structure of the finishing agent. Information on uses may be found in the publications cited earlier.

In the Examples which follow, parts are by weight.

#### EXAMPLE 1.

##### a) Manufacture of the nickel-containing catalyst.

A column is filled with 1,000 parts of cation exchanger, which is allowed to stand in 1,000 parts of water for 15 minutes. 500 parts of 10 per cent strength by weight hydrochloric acid are then added, the column is left to stand for 20 minutes and the cation exchanger is then washed neutral with distilled water. 3,400 parts of a 10 per cent strength by weight solution of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  are then charged onto the activated exchanger. When the solution leaving the column no longer reacts acid, the uptake of nickel salt has ended. The exchanger charge is washed neutral with water and then washed free from water with dioxane or the fluid alcohol II to be used for the carbamate synthesis. The exchanger is now ready to use and contains 0.065 part of nickel per part of exchanger.

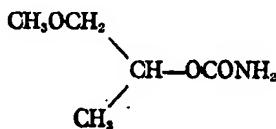
##### b) Reaction



5 A mixture of 300 parts of urea, 684 parts of methylglycol and 18 parts of a cation exchanger which is commercially available under the registered name Amberlite 200 and, having been treated in accordance with Example 1a), contains nickel, is heated, with stirring, to the reflux temperature (130° C.) in the course of 20 minutes, in a stirred apparatus equipped with a reflux condenser. After reaching the reflux temperature, a slight stream of nitrogen bubbles is passed through the reaction mixture. The reflux temperature rises to from 148 to 150° C. in the course of 5.5 hours. The reaction temperature is then kept at 149° C. After a total reaction time of 10 7 hours, the reaction solution is cooled to about 120° C. and the exchanger is filtered off. 10

15 Excess methylglycol is distilled off under reduced pressure. 586 parts of methoxyethyl carbamate are obtained. This corresponds to a yield of 98.5% of theory, based on urea employed. On distilling the carbamate at a pressure of 0.1 mm Hg, a distillation residue of only 0.8% by weight is left. The carbamate has a boiling range of 15 from 96 to 98° C. at 0.1 mm Hg. 15

#### EXAMPLE 2.



20 300 parts of urea, 810 parts of methoxyisopropanol and 18 parts of a cation exchanger which is commercially available under the registered name Amberlite 200 and, having been treated in accordance with Example 1a), contains nickel, are mixed in a stirred apparatus and the mixture is heated to the reflux temperature (125° C.) in the course of 30 minutes, whilst stirring. The mixture is then heated at the reflux temperature for 8 hours, whilst a stream of nitrogen is passed through it. The reflux temperature rises to 140° C. After the reaction solution has cooled, the exchanger is filtered off and excess methoxyisopropanol is distilled off under reduced pressure. 652 parts of methoxyisopropyl carbamate (98% of theory, based on urea) are obtained. 25 The carbamate boils at 92° C. under 0.2 mm Hg and leaves a distillation residue of only 0.9% by weight. Melting point=53—54° C. 25

#### EXAMPLE 3.

30  $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OCONH}_2$ . 30

35 300 parts of urea, 810 parts of ethylglycol and 15 parts of a cation exchanger which is commercially available under the registered name Amberlyst 15 and, having been treated in accordance with Example 1a), contains nickel, are heated to the reflux temperature (138° C.) in a stirred vessel. After 2 hours, the reflux temperature rises to 148° C. The reaction mixture is kept at this temperature for a further 8 hours, 40 whilst a slight stream of nitrogen is passed through it. After filtering off the exchanger, excess ethylglycol is distilled off under reduced pressure. 645 parts of ethoxyethyl carbamate are obtained. This corresponds to 97% of theory, based on urea. On distilling the crude carbamate in a high vacuum, the end product distils at 110° C. under 0.2 mm Hg. A distillation residue of 0.9% is left. 40

#### EXAMPLE 4.

$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OCONH}_2$ .

45 60 parts of urea are mixed with 177 parts of butylglycol and 3 parts of a cation exchanger which is commercially available under the registered name Lewatit CA 9259 and, having been treated in accordance with Example 1a), contains nickel, in a stirred apparatus. The mixture is heated to 135° C., whilst stirring. It is then heated for 10 hours at 140° C. After cooling, the mixture is filtered and the excess butylglycol is distilled from the filtrate under reduced pressure. 158 parts of n-butoxyethyl carbamate (corresponding to 98% of theory, based on urea) are obtained. On distillation of the end product in a high vacuum, a residue of only 0.9% by weight is left. The pure butoxyethyl carbamate has a boiling point of 118—120° C. at 0.2 mm Hg. 50

## EXAMPLE 5.



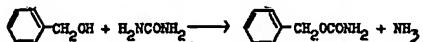
600 parts of urea, 2,916 parts of butyldiglycol and 28 parts of a cation exchanger which is commercially available under the registered name Amberlite 200 and, having been treated in accordance with Example 1a), contains nickel, are heated for 10 hours at 150° C. in a stirred vessel, whilst a slight stream of nitrogen is passed through the mixture. The exchanger is then filtered off whilst the solution is still hot and the excess butyldiglycol is distilled off under reduced pressure. 1,988 parts of butyldiglycol carbamate are obtained. This corresponds to a yield of 97%, based on the amount of urea employed. The carbamate has a boiling range of 146—148° C. at 0.2 mm Hg and leaves a distillation residue of 1.1% by weight.

## EXAMPLE 6.



A mixture of 120 parts of urea, 741 parts of butyltriglycol and 5 parts of a cation exchanger which is commercially available under the registered name Amberlite 200 and, having been treated in accordance with Example 1a), contains nickel, is heated for 10 hours at 145° C. in a stirred vessel whilst a slight stream of nitrogen is passed through the mixture. The exchanger is filtered off whilst the reaction solution is hot and the excess butyltriglycol is distilled off under reduced pressure. 493 parts of butyltriglycol carbamate are obtained. This corresponds to a yield of 99% of theory, based on urea. The carbamate has a boiling range of 172—175° C. at from 0.2 to 0.3 mm Hg.

## EXAMPLE 7.



A mixture of 240 parts of urea, 778 parts of benzyl alcohol and 11 parts of a cation exchanger which is commercially available under the registered name Amberlyst 15 and, having been treated in accordance with Example 1a), contains nickel, is heated to the reflux temperature (131° C.) in a stirred vessel. In the course of 6 hours, the reflux temperature rises to 149° C. The reaction mixture is then heated at 149—150° C. for a further 2 hours. After filtering off the exchanger, excess benzyl alcohol is removed by distillation under reduced pressure. 586 parts of benzyl carbamate are obtained. This corresponds to a yield of 97% of theory, based on urea. Benzyl carbamate boils at 116—118° C. under from 0.3 to 0.4 mm Hg. Melting point=75—76° C. On distillation, a residue of 1% by weight is left.

## EXAMPLE 8.



A mixture of 918 parts of hexyl alcohol, 300 parts of urea and 14 parts of a cation exchanger which is commercially available under the registered name Amberlite 200 and, having been treated in accordance with Example 1a), contains nickel, is heated to 130° C. whilst stirring. The temperature is then raised to 150° C. in the course of 6 hours and maintained thereat for a further 4 hours. After filtering off the exchanger, excess hexyl alcohol is distilled off under reduced pressure. 680 parts of hexyl carbamate (94% of theory) are obtained. Melting point=56—57° C.

## EXAMPLE 9.



410 parts of 1,3-propanediol, 180 parts of urea and 11 parts of a cation exchanger which is commercially available under the registered name Amberlite 200 and, having been treated in accordance with Example 1a), contains nickel, are heated at 150° C. for 10 hours in a stirred apparatus, whilst a slight stream of nitrogen is passed through the mixture. The exchanger is then filtered off and excess propanediol is

evaporated off under reduced pressure. On distillation in a high vacuum at 138—140° C. and 0.1 mm Hg, 350 parts of  $\gamma$ -hydroxypropyl carbamate (98% of theory) are obtained. The distillation in a high vacuum leaves a residue of only 0.9% by weight.

EXAMPLE 10.

5

$C_1H_{35}OCONH_2$ .

5

A mixture of 256 parts of heptadecyl alcohol, 60 parts of urea and 5 parts of a cation exchanger which is commercially available under the registered name Amberlite 200 and, having been treated in accordance with Example 1, contains nickel, is heated in a stirred vessel to 140—145° C., whilst stirring. After filtering off the exchanger whilst the reaction solution is hot, 280 parts of heptadecyl carbamate are obtained. This corresponds to a yield of 94% of theory. The product has a melting point of 53—54° C.

10

EXAMPLE 11.

15

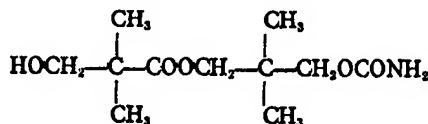
A mixture of 659 parts of phenylglycol, 180 parts of urea and 9 parts of a cation exchanger which is commercially available under the registered name Amberlyst 15 and, having been treated in accordance with Example 1a), contains nickel, is heated to 130° C. whilst stirring. The temperature is raised to 150° C. in the course of 6 hours and is then maintained thereat for a further 4 hours. After filtering off the exchanger whilst the reaction solution is hot, the filtrate is cooled to room temperature. After standing for several hours, the phenylglycol carbamate which has precipitated is filtered off. After evaporating off the excess phenylglycol under reduced pressure, a total of 499 parts of phenylglycol carbamate are obtained. This corresponds to a yield of 92% of theory. Melting point = 105—106° C.

15

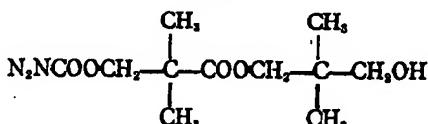
20

25

EXAMPLE 12.



and



612 parts of neopentylglycol hydroxypivalate, 180 parts of urea and 9 parts of a cation exchanger which is commercially available under the registered name Amberlite 200 and, having been treated in accordance with Example 1a), contains nickel, are heated to 130° C. in a stirred apparatus, whilst a slight stream of nitrogen is passed through the mixture. The temperature is raised to 150° C. in the course of 10 hours. After filtering off the exchanger whilst the reaction solution is hot, 714 parts of a 1:1 mixture of neopentylglycol hydroxypivalate carbamate isomers of  $n_D^{20}=1.4613$  are obtained. This corresponds to a yield of 96% of theory.

30

35

35

EXAMPLE 13.

40

810 parts of a polyether-diol having the structure  $H(OCH_2CH_2)_{12}OH$ , 60 parts of urea and 3.6 parts of a cation exchanger which is commercially available under the registered name Amberlite 200 and, having been treated in accordance with Example 1a), contains nickel, are mixed, and heated to 130° C., in a stirred apparatus. The temperature is then raised to 150° C. in the course of 6 hours and kept thereat for a further 4 hours. The exchanger is filtered off whilst the reaction solution is hot.

40

805 parts of carbamate of the formula  $H-(OCH_2CH_2)_{12}OCONH_2$ , of melting point 32-34° C., are obtained. This corresponds to a yield of 94% of theory. The product is colorless and pasty.

EXAMPLE 14.

5



5

414 parts of a polyether-diol having the structure  $H-(OCH_2CH_2)_nOH$ , 60 parts of urea and 4 parts of a cation exchanger which is commercially available under the registered name Amberlite 200 and, having been treated in accordance with Example 1a), contains nickel, are heated to 130° C. The temperature is raised to 150° C. in the course of 6 hours and is then maintained thereat for a further 4 hours. After filtering off the exchanger, 415 parts (91% of theory) of monocarbamate of the formula  $H-(OCH_2CH_2)_nOCONH_2$  are obtained. Refractive index  $n_D^{20}=1.4708$ .

EXAMPLE 15 (USE).

595 parts of the methoxyethyl carbamate manufactured according to Example 1b), 750 parts of a 40 per cent strength by weight formaldehyde solution and 6 parts of a 50 per cent strength by weight sodium hydroxide solution are heated in a stirred apparatus for 3 hours at 50° C., whilst stirring. This solution is neutralized with dilute sulfuric acid and then made up to 1,790 parts by water. This then constitutes a 50 per cent strength by weight solution of dimethylolmethoxyethyl carbamate.

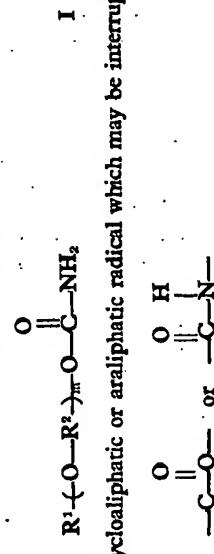
A bleached and mercerized cotton fabric (poplin) weighing 125 g/square meter was impregnated, on a padder, with a solution prepared by diluting 150 parts of a 50 per cent strength by weight aqueous solution of  $N,N$ -dimethylolmethoxyethyl carbamate, 1 part of a reaction product of 7 moles of ethylene oxide with 1 mole of isooctyl-phenol and 30 parts of magnesium chloride hexahydrate to 1,000 parts by volume with water. The impregnated fabric is squeezed off to a wet pick-up of from 70 to 75% and is dried to 6-8% residual moisture content on a tenter frame at 110° C. The treated fabric is then heated for 4 minutes at 160° C. on a tenter frame. The technological data are summarized in the Table which follows.

TABLE

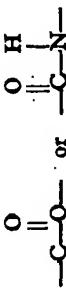
	Untreated fabric	Finished fabric
Dry crease angle according to DIN 53,890 (warp + filling) (°C)	122°	253°
Dry crease angle after 3 machine washes, each of 120 minutes, at the boil (warp + filling) (°C)	121°	248°
Wet crease angle according to DIN 53,891 (warp + filling) (°C)	129°	252°
Wet crease angle according to DIN 53,891, after 3 machine washes, each of 120 minutes, at the boil (warp + filling) (°C)	128°	248°
Wrinkle-resist test according to AATCC 86-1964-T	1.5	4.5
Tensile strength, 40 × 100 mm (DIN 53,857) finish, filling, in kg	40.0	27.5
After 1 alternating chlorination treatment (AATCC 92-1971) Tensile strength, 40 × 100 mm, filling, in kg	40.5	27.3
After 3 alternating chlorination treatments (AATCC 92-1971) Tensile strength, 40 × 100 mm, filling, in kg	40.0	27.0
After 5 alternating chlorination treatments (AATCC 92-1971) Tensile strength, 40 × 100 mm, filling, in kg	39.2	27.0

## WHAT WE CLAIM IS:—

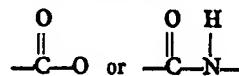
1. A process for the manufacture of a carbamate of the formula



5 where  $\text{R}^1$  is an aliphatic, cycloaliphatic or araliphatic radical which may be interrupted by one or more



groups and/or oxygen atoms,  $\text{R}^2$  is an aliphatic radical of at least 2 carbon atoms which is optionally interrupted by one or more



groups and/or oxygen atoms, or is



5 where the individual R's are identical or different and each is a cycloaliphatic, 5 araliphatic or aromatic radical, and n is an integer from 2 to 6, and m is 0 or a positive integer, or R<sup>1</sup> is



or phenyl or—if m is a positive integer—hydrogen, by reaction of an alcohol with urea in the presence of nickel, wherein an alcohol of the formula

10



II

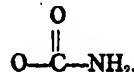
10

where R<sup>1</sup>, R<sup>2</sup> and m have the above meaning, is reacted with urea in the presence of an ion exchanger containing nickel.

15

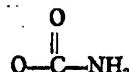
2. A process as claimed in claim 1, wherein the alcohol of formula II contains one or more OH groups and the reaction is carried out with from 0.5 to 1 mole of urea per mole of starting material II to replace one OH group by

15



3. A process as claimed in claim 1, wherein the alcohol of formula II contains two or more OH groups and the reaction is carried out with from 2 to 2.5 moles of urea per mole of starting material II to replace two OH groups by

20



20

4. A process as claimed in any of claims 1 to 3, wherein the reaction is carried out at from 100 to 160° C.

5. A process as claimed in claim 4, wherein the reaction is carried out at from 125 to 150° C.

25

6. A process as claimed in any of claims 1 to 5, wherein the reaction is carried out in the presence of an organic solvent which is inert under the reaction conditions.

25

7. A process as claimed in any of claims 1 to 6, wherein the reaction is carried out with a phenolic resin, a polystyrenesulfonic acid resin, a bifunctional condensation resin, a polystyrenephosphonic acid resin, a polystyrenephosphinic acid resin, a resorcinol resin or an aliphatic or aromatic carboxylic acid resin as the exchanger.

30

8. A process as claimed in any of claims 1 to 7, wherein the reaction is carried out with a charge of from 0.01 to 0.2 part by weight of nickel per part by weight of exchanger, and with from 0.01 to 0.25 per cent by weight of exchanger per part by weight of urea.

35

9. A process as claimed in any of claims 1 to 8, wherein an alcohol of the formula

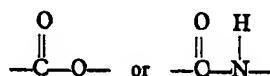
30



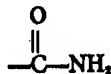
II

35

is employed, where R<sup>1</sup> is alkyl of up to 7 carbon atoms optionally interrupted by one or two oxygen atoms or one

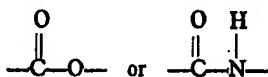


group or substituted by hydroxyl, or is cycloalkyl of 5 or 6 carbon atoms or aralkyl of 7 to 12 carbon atoms or phenyl or



5 or (provided that m is not zero) hydrogen, and R<sup>2</sup> is alkylene of 2 to 7 carbon atoms optionally interrupted by one or two oxygen atoms or one

5



group or substituted by hydroxyl, and m is zero or an integer from 1 to 28.

10 10. A process for the manufacture of a carbamate carried out substantially as described in any of the foregoing Examples.

11. Carbamates when manufactured by a process as claimed in any of claims 1 to 10.

10

12. A methylolated carbamate when obtained by reaction of a carbamate as claimed in claim 11 with formaldehyde.

13. A textile finishing agent comprising a methylolated carbamate as claimed in claim 12 manufactured without purification of the carbamate manufactured by the process of any of claims 1 to 10.

15

J. Y. & G. W. JOHNSON,  
Furnival House, 14-18, High Holborn, London, WC1V 6DE,  
Chartered Patent Agents,  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.